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Oxidation and Reduction

J. S. LANGREHR



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NATIONAL SCIENCE CURRICULUM MATERIALS



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Oxidation and Reduction

J. S. Langrehr

Findon High School, South Australia

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Contents

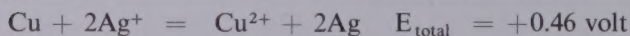
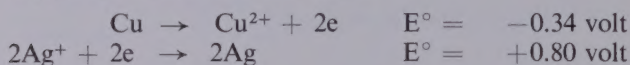
Periodic Table	v
International Atomic Weights	vi
Introduction	1
Some Early Ideas	1
Oxidation Number	4
Rules for assigning Oxidation numbers	6
Definitions in terms of Oxidation number	8
Balancing Redox reactions	9
Harnessing the Electron Transfer in Redox Reactions	14
Standard half-cells or electrodes	17
Standard Electrode Potentials	19
Table of Standard Oxidation Potentials	22
Table of Standard Reduction Potentials	23
Use of Standard Electrode Potentials	25
To predict the likelihood of a reaction between an oxidiser and a reducer	26
To predict the E.M.F. of a cell	28
Electrolysis	31
Electrolysis of aqueous solutions	33
Electroplating	38
Quantitative relations in electrolysis	40
Redox—The Present and Future	42
Reading List	43
Questions and Problems	44
Index	47

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Figure 9 is by courtesy of the Royal Australian Navy and figure 15 has been reproduced by permission of Copper Refineries Pty. Ltd., Townsville.

The cover photo shows the redox reaction between copper and silver nitrate solution



Since E_{total} is positive a reaction is possible. Silver will be deposited on the copper strip and copper ions will go into solution colouring it blue.

1.008

PERIODIC TABLE

[illegible]

³ Li 6.94	⁴ Be 9.01	¹¹ Na 23.0	¹² Mg 24.3	¹⁹ K 39.1	²⁰ Ca 40.1	³⁷ Rb 85.5	³⁸ Sr 87.6	⁵⁵ Cs 132.9	⁵⁶ Ba 137.3	⁸⁷ Fr (223)	⁸⁸ Ra (226)
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21	22	23	24	25	26	27	28	29	30
Sc 45.0	Ti 47.9	V 50.9	Cr 52.0	Mn 54.9	Fe 55.8	Co 58.9	Ni 58.7	Cu 63.5	Zn 65.4
39	40	41	42	43	44	45	46	47	48
Y 88.9	Zr 91.2	Nb 92.9	Mo 95.9	Tc (99)	Ru 101.1	Rh 102.9	Pd 106.4	Ag 107.9	Cd 112.4
57-71	72	73	74	75	76	77	78	79	80
La-Lu	Hf 178.5	Ta 180.9	W 183.9	Re 186.2	Os 190.2	Ir 192.2	Pt 195.1	Au 197.0	Hg 200.6

57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
138.9	140.1	140.9	144.2	(145)	150.4	152.0	157.2	158.9	162.5	164.9	167.3	168.9	173.0	175.0

89	Ac	227
90	Th	232.0
91	Pa	231
92	U	238.0
93	Np	237
94	Pu	242
95	Am	243
96	Cm	248
97	Bk	247
98	Cf	249
99	Es	254
100	Fm	253
101	Md	256
102	No	254
103	Lw	257

Parenthetical values are mass numbers of the isotopes with longest half-lives

INTERNATIONAL ATOMIC WEIGHTS

(Atomic Weights relative to $^{12}\text{C} = 12$ exactly)

Atomic Number	Name	Symbol	Atomic Weight	Atomic Number	Name	Symbol	Atomic Weight
1	Hydrogen	H	1.008	31	Gallium	Ga	69.72
2	Helium	He	4.003	32	Germanium	Ge	72.59
3	Lithium	Li	6.939	33	Arsenic	As	74.92
4	Beryllium	Be	9.012	34	Selenium	Se	78.96
5	Boron	B	10.81	35	Bromine	Br	79.91
6	Carbon	C	12.01	36	Krypton	Kr	83.80
7	Nitrogen	N	14.01	37	Rubidium	Rb	85.47
8	Oxygen	O	16.00	38	Strontium	Sr	87.62
9	Fluorine	F	19.00	39	Yttrium	Y	88.91
10	Neon	Ne	20.18	40	Zirconium	Zr	91.22
11	Sodium	Na	22.99	41	Niobium	Nb	92.91
12	Magnesium	Mg	24.31	42	Molybdenum	Mo	95.94
13	Aluminium	Al	26.98	43	Technetium*	Tc	(99)
14	Silicon	Si	28.09	44	Ruthenium	Ru	101.1
15	Phosphorus	P	30.97	45	Rhodium	Rh	102.9
16	Sulphur	S	32.06	46	Palladium	Pd	106.4
17	Chlorine	Cl	35.45	47	Silver	Ag	107.9
18	Argon	Ar	39.95	48	Cadmium	Cd	112.4
19	Potassium	K	39.10	49	Indium	In	114.8
20	Calcium	Ca	40.08	50	Tin	Sn	118.7
21	Scandium	Sc	44.96	51	Antimony	Sb	121.8
22	Titanium	Ti	47.90	52	Tellurium	Te	127.6
23	Vanadium	V	50.94	53	Iodine	I	126.9
24	Chromium	Cr	52.00	54	Xenon	Xe	131.3
25	Manganese	Mn	54.94	55	Caesium	Cs	132.9
26	Iron	Fe	55.85	56	Barium	Ba	137.3
27	Cobalt	Co	58.93	57	Lanthanum	La	138.9
28	Nickel	Ni	58.71	58	Cerium	Ce	140.1
29	Copper	Cu	63.54	59	Praseodymium	Pr	140.9
30	Zinc	Zn	65.37	60	Neodymium	Nd	144.2

*Unstable elements

Parenthetical numbers refer to the mass number (not the atomic weight) of the isotope with the longest half-life.

INTERNATIONAL ATOMIC WEIGHTS

(Atomic Weights relative to $^{12}\text{C} = 12$ exactly)

Atomic Number	Name	Symbol	Atomic Weight	Atomic Number	Name	Symbol	Atomic Weight
61	Promethium*	Pm	(145)	86	Radon*	Rn	(222)
62	Samarium	Sm	150.4	87	Francium*	Fr	(223)
63	Europium	Eu	152.0	88	Radium*	Ra	(226)
64	Gadolinium	Gd	157.3	89	Actinium*	Ac	(227)
65	Terbium	Tb	158.9	90	Thorium*	Th	232.0
66	Dysprosium	Dy	162.5	91	Protactinium*	Pa	(231)
67	Holmium	Ho	164.9	92	Uranium*	U	238.0
68	Erbium	Er	167.3	93	Neptunium*	Np	(237)
69	Thulium	Tm	168.9	94	Plutonium*	Pu	(242)
70	Ytterbium	Yb	173.0	95	Americium*	Am	(243)
71	Lutetium	Lu	175.0	96	Curium*	Cm	(248)
72	Hafnium	Hf	178.5	97	Berkelium*	Bk	(247)
73	Tantalum	Ta	180.9	98	Californium*	Cf	(249)
74	Tungsten	W	183.9	99	Einsteinium*	Es	(254)
75	Rhenium	Re	186.2	100	Fermium*	Fm	(253)
76	Osmium	Os	190.2	101	Mendelevium*	Md	(256)
77	Iridium	Ir	192.2	102	Nobelium*	No	(254)
78	Platinum	Pt	195.1	103	Lawrencium*	Lw	(257)
79	Gold	Au	197.0	104	(Kurchatovium)		
80	Mercury	Hg	200.6				
81	Thallium	Tl	204.4				
82	Lead	Pb	207.2				
83	Bismuth	Bi	209.0				
84	Polonium*	Po	(210)				
85	Astatine*	At	(210)				

*Unstable elements

Parentetical numbers refer to the mass number (not the atomic weight) of the isotope with the longest half-life.

After reading this booklet you should know something of:

- the historical development of the concepts of oxidation and reduction namely loss and gain of oxygen content, loss and gain of electrons and increase and decrease in oxidation number;
- the historical development of the electro-chemical cell;
- the construction and functioning of an electro-chemical cell;
- the construction of standard half cells;
- standard electrode potentials, their measurement and their values relative to each other;
- electrolysis reactions in molten and aqueous solutions of electrolytes;
- the essentials of electroplating; and
- the overall importance of redox reactions in nature, in the laboratory and in industry.

You should be able to:

- calculate the oxidation number of atoms in molecules and ions;
- use oxidation number changes to:
 - identify oxidation and reduction; and
 - to balance redox equations;
- balance a half equation and combine it with another half equation to give a complete equation; and
- use standard electrode potentials to:
 - predict the likelihood of a redox reaction; and
 - calculate the E.M.F. of a cell.

Introduction

Do you realise that the process of oxidation is occurring within the cells of your body at this very moment? Have you ever stopped to think that all plants, animals and minerals on the surface of the Earth are continually bathed in the oxygen of the atmosphere and that this invisible gas is ever ready to combine with substances within them and hence oxidise them?

You can probably think of many examples where oxygen-containing substances such as carbon dioxide, water, hydrogen peroxide and oxy-acids react with other substances and transfer some of their oxygen to them, whether it be in nature, in the laboratory or in industry. As you think you may ask yourself some interesting questions. What is rust and how does it form? Why doesn't aluminium rust and corrode itself away like iron? Are oxygen atoms the only atoms that can oxidise substances? How does the oxidation process within a flashlight cell or car battery produce electricity?

The answers to these and other questions concerning this fundamental chemical process oxidation, should unfold as we look into the explanations given us by the concepts and principles that have evolved during the last two hundred years.

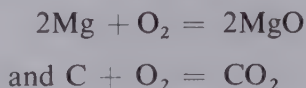
Some Early Ideas

Probably one of the first men to have used and understood such words as oxidation, oxidise and oxide was Antoine Lavoisier (1743-94) a French chemist.

Lavoisier's discovery of what actually happens during the burning of a substance in air has been considered as being one of the greatest discoveries in chemistry. He lived at a time when scientists believed that a substance when burned in air lost something called *phlogiston*, leaving behind a *calx*. Through experimentation Lavoisier freed the minds and imagination of his fellow men so that they too understood that oxygen was taken from the air

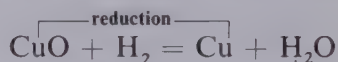
during the processes of burning and corrosion, with a resulting increase in weight of the oxidised substance.

Because oxygen combined with most metals and non-metals to form oxides it was not surprising that such reactions were called oxidation reactions. In the reactions



magnesium and carbon were said to be oxidised because they had combined with oxygen.

It was not long before it became apparent that some chemical reactions involved the removal or **reduction** of the oxygen content from oxygen containing substances and in this respect they were the reverse of oxidation reactions. These reactions became known as reduction reactions. Cupric oxide is reduced to copper by passing hydrogen gas over the heated cupric oxide.

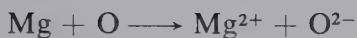


Even using these simple definitions of oxidation and reduction, it became obvious that when the oxygen content of one substance was reduced it automatically followed that the substance removing this oxygen, was itself oxidised.

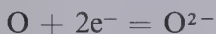
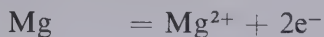
Oxidation and reduction reactions then, were no longer thought of as being separate, independent reactions but rather as *converse, simultaneous reactions*. A substance reducing the oxygen content of another became known as the **reducer** and the substance supplying the oxygen as the **oxidiser**. These original definitions, which are still of use today to identify oxidation and reduction in some organic chemical reactions, were retained for many years.

At the beginning of this century when the theories of atomic structure and bonding were developed, the definitions were extended to take into account the changes that occur within atoms that are participating in oxidation-reduction reactions. The newer, broader definitions were in no way contrary to the former definitions but were merely more specific as to what was happening at the atomic level in the light of new discoveries.

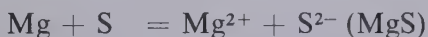
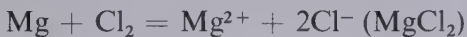
Consider the oxidation of magnesium to magnesium oxide and the subsequent changes in the electronic configurations of the atoms before and after they react.



The magnesium atoms which have been oxidised have *lost electrons* in the process. One can get a better idea of the *transfer* of electrons from the magnesium atoms to the oxygen atoms by writing the equation in two halves or *half equations*.



Many other non-metals were discovered to be capable of removing electrons from magnesium atoms. For example

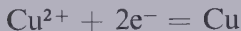


Although these reactions were not thought of as being oxidation reactions at first, their basic similarity in the removal of electrons from the magnesium atoms resulted in them being classified as *reduction-oxidation* or **redox** reactions also.

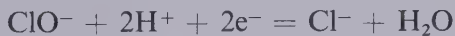
Oxidation was defined as the *loss of electrons from a substance*. Quite naturally the converse reaction, *reduction*, was defined as the *gain of electrons* by a substance. Using these broader definitions it was quite clear that in the above reactions oxygen, chlorine and sulphur are reduced to their ions which also exist in the one product that forms. The concept that an *oxidising agent* had to contain oxygen was extended to a more general definition of a *substance capable of accepting electrons; i.e. an electron acceptor*. A *reducing agent* on the other hand was not necessarily a metal but rather any substance that had the *ability to give up electrons; i.e. an electron donor*.

The range of substances that could now be classified as an oxidiser or reducer grew rapidly, for now oxidisers (electron acceptors) included such things as:

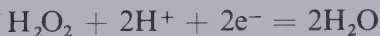
(a) positive ions e.g.



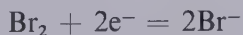
(b) negative ions e.g.



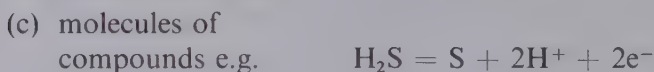
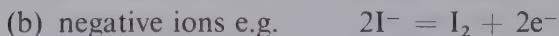
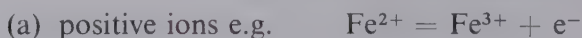
(c) molecules of
compounds e.g.



(d) molecules of
elements e.g.



and reducers (electron donors) such things as:



Oxidation Number

The identification of oxidation and reduction in terms of the loss and gain of electrons was easy to apply to *electron transfer* reactions where the reacting substances formed positive and negative ions. However it was apparent that oxidation reactions could occur, in which electrons were only *shared* between combining atoms. In the following reactions the electrons of the carbon and sulphur atoms are not completely transferred to the oxygen atoms although the reactions are quite definitely redox reactions.



At first, this type of reaction seemed to have little similarity to complete electron transfer reactions. A *unifying concept* was needed that could be used to identify redox in a reaction whether it involved the complete transfer of electrons from one atom to another or only the partial shift of electrons shared between atoms, towards the more 'electron seeking' of the atoms. This concept became known as **oxidation number**.

The *oxidation number* of an atom can be defined as the *imaginary ionic charge an atom would have if the electron pairs it is sharing with other atoms were in fact transferred completely to the atoms with the higher electron affinity*.

In a molecule of hydrogen chloride for example, the electron cloud between the hydrogen and chlorine atom is displaced towards the chlorine atom which has a stronger affinity for electrons than the hydrogen atom.

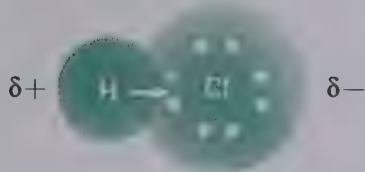


Figure 1. The displacement of the electron cloud in a polar HCl molecule

Hence the molecule is polarized, with the chlorine end of the molecule gaining a fractional negative charge (δ^-) and the hydrogen end a fractional positive charge (δ^+). If we consider that the shared pair of electrons is completely displaced to the chlorine atom then its 'make believe' ionic charge or oxidation number would be -1 , $\text{Cl}^{(-1)}$, as it has ideally gained the electron of the hydrogen atom. The oxidation number of the hydrogen atom would be $+1$, $\text{H}^{(+1)}$. Can you predict the oxidation number of each chlorine atom in a molecule of chlorine Cl_2 ?

Figure 2 shows the direction of displacement of shared electron pairs between atoms and the resulting oxidation numbers assigned to the atoms involved.

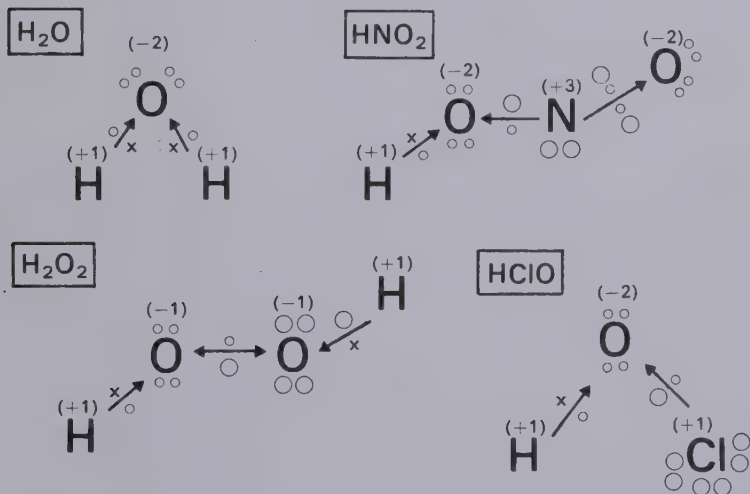


Figure 2. Resulting oxidation numbers of atoms after shared electron pairs move to the more electronegative atom

When you have calculated the oxidation number of an atom in a substance, its magnitude and sign is generally written directly above the symbol for the atom. For example in $\text{Na}_2\text{Cr}_2\text{O}_7$ the oxidation number of *each* sodium atom is $+1$, of *each* chromium atom $+6$ and *each* oxygen atom -2 . Do you notice anything about the *sum* of the oxidation numbers of *all* of the atoms in a formula? What can you say about the sum of the oxidation numbers of all of the atoms in a 'many atom' ion such as $\text{MnO}_4^{(-)}$?

You are probably wondering how to calculate oxidation numbers of atoms in formulas such as $\text{Na}_2\text{S}_2\text{O}_3$, FeSO_4 , Mn_2O_7 and $\text{Cr}_2\text{O}_7^{2-}$. The first chemists who carried out such calculations had to have a knowledge of the relative electron affinities of the atoms within ions and molecules as well as a knowledge of how these atoms were bonded together. Their calculations would look like those in figure 2.

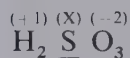
However after many such tedious calculations they recognised, just as you may have from the examples in figure 2, that some atoms had the same oxidation number, regardless of the ion or molecule they were in.

Oxygen atoms seemed to have a constant oxidation number of -2 and hydrogen atoms an oxidation number of $+1$. There are very good reasons why these atoms have these oxidation numbers if you stop to think about it. Other constant features were noted, such as the oxidation numbers of atoms in uncombined elements and in monatomic ions and also the sum of the oxidation numbers of all of the atoms in neutral molecules and in poly-atomic ions.

Rules for Assigning Oxidation Numbers

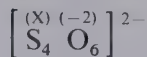
- (1) In uncombined elements each atom has an oxidation number of zero; e.g. $\overset{(0)}{\text{Na}}$, $\overset{(0)}{\text{S}_8}$, $\overset{(0)}{\text{N}_2}$.
- (2) The oxidation number of a monatomic ion is equal to the charge on the ion; e.g. $\overset{(+1)}{\text{Na}^+}$, $\overset{(+3)}{\text{Fe}^{3+}}$, $\overset{(-2)}{\text{S}^{2-}}$.
- (3) Oxygen has an oxidation number of -2 in compounds (except in peroxides where it is -1 ; e.g. $\overset{(-1)}{\text{H}_2\text{O}_2}$, $\overset{(-1)}{\text{BaO}_2}$ and in $\overset{(+2)}{\text{F}_2\text{O}}$ where it is $+2$).
- (4) Hydrogen has an oxidation number of $+1$ in compounds (except in ionic hydrides where it is -1 ; e.g. $\overset{(-1)}{\text{NaH}}$, $\overset{(-1)}{\text{CaH}_2}$).
- (5) The *sum of the oxidation numbers of all atoms*:
 - (a) in a neutral molecule is zero.
 - (b) in a poly-atomic ion is equal to the charge on the ion.

The examples below illustrate the application of these rules in calculating the oxidation number of the atoms underlined.



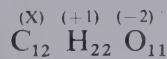
$$2(+1) + (x) + 3(-2) = 0$$

$$x = +4$$



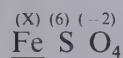
$$4(x) + 6(-2) = -2$$

$$x = +2\frac{1}{2}$$



$$12(x) + 22(+1) + 11(-2) = 0$$

$$x = 0$$



$$(x) + (6) + 4(-2) = 0$$

$$x = +2$$



$$(x) + 3(+1) = 0$$

$$x = -3$$

Note

- (1) The oxidation number of an atom in a compound may be positive or negative, and may be zero, a whole number or a fraction.
- (2) Oxidation numbers are not intended to be a representation of the true state of affairs. For example in $\text{MnO}_4^{(-)}$, the manganese atom does not have a real charge of $+7$ on it but rather seven of its electrons have been displaced towards the four surrounding oxygen atoms.
- (3) Oxidation number should not be confused with the valence of an atom as indicated in the following example of the bromine substitution compounds of methane. Here the valence of carbon is 4 throughout, while the oxidation number varies from -4 to $+4$.

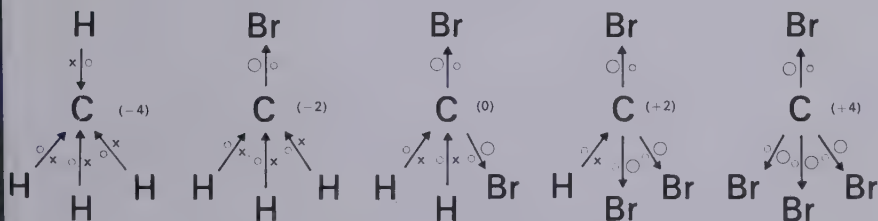
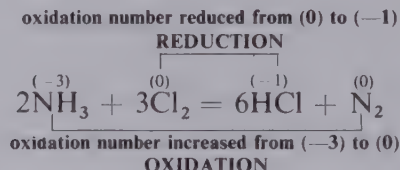


Figure 3. The valence of carbon in the compounds is 4, but the oxidation number of carbon changes from -4 to $+4$

Definitions in Terms of Oxidation Number

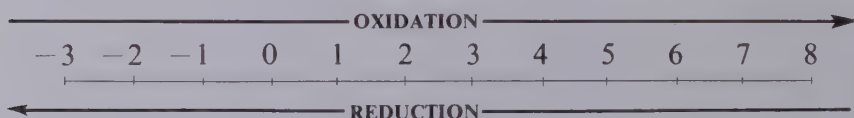
In a molecular redox reaction where a complete transfer of electrons from atom to atom does not occur, the atoms whose oxidation numbers have changed from what they were in a reactant to what they are in a product are the atoms whose electrons have been partially displaced. Not only are these atoms said to be oxidised and reduced, but also the complete substance containing these atoms has been oxidised and reduced.



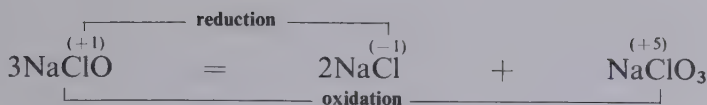
Oxidation of an atom (and hence the molecule or ion containing it) involves the algebraic increase in oxidation number of that atom.

Reduction of an atom (and hence the molecule or ion containing it) involves the algebraic reduction in oxidation number of that atom.

As in previous definitions the oxidiser is the substance reduced. An atom whose oxidation number is initially zero and has it changed to say -2 on reaction, has numerically 'gained' an oxidation number but the gain involves an algebraic decrease in oxidation and hence the atom has been reduced. This idea of an algebraic increase and decrease is summarized on the scale below.



It can happen that an atom in a compound has its oxidation number both increased and decreased on forming products. An example of this unusual case of a substance being both oxidised and reduced at the same time in a reaction is found in the decomposition of sodium hypochlorite by heat to form sodium chloride and sodium chlorate. The process is called **auto-oxidation** or **disproportionation**.



Balancing Redox Reactions

The balancing of equations for redox reactions is based on the fact that in these reactions the number of electrons lost by the reducer is equal to the number of electrons gained by the oxidiser. If oxidation numbers are being used to trace this electron transfer, then it is also true to say that the total increase in oxidation number of the reducer must equal the total decrease in oxidation number of the oxidiser.

Redox equations can be balanced by one of two methods namely the *half equation method* or the *change in oxidation number method* but whatever method you decide to use, you will have to know what products the reactants form, or make a prediction as to what products could form. Most oxidisers or reducers can form only one or two possible products in a redox reaction. The one that actually forms is dependent on such conditions as concentration, temperature and acidity.

For example the oxidising permanganate ion MnO_4^- , in which Mn has an oxidation number (O.N.) of +7, can form Mn^{2+} ions (in which Mn has O.N. of +2), MnO_2 (in which Mn has O.N. of +4), or MnO_4^{2-} (in which Mn has O.N. of +6) depending on the acidity of the solution. The nitrate ion NO_3^- (O.N. of nitrogen = +5) can form NO_2 (O.N. of nitrogen +4), NO (O.N. of nitrogen +2) or N_2O (O.N. of nitrogen +1) depending on the concentration of the solution.

Some common oxidisers that are used in the laboratory (and the product they will possibly form) include such things as $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$, $\text{NO}_3^-/\text{NO}_2$, Cl_2/Cl^- , $\text{H}_2\text{O}_2/\text{H}_2\text{O}$, IO_3^-/I_2 and $\text{MnO}_4^-/\text{Mn}^{2+}$.

On the other hand some common reducers and their oxidised form are $\text{C}_2\text{O}_4^{2-}/\text{CO}_2$, $\text{Fe}^{2+}/\text{Fe}^{3+}$, I^-/I_2 , $\text{Sn}^{2+}/\text{Sn}^{4+}$, $\text{SO}_2/\text{SO}_4^{2-}$, Al/Al^{3+} , $\text{H}_2\text{O}_2/\text{O}_2$, $\text{HSO}_3^-/\text{HSO}_4^-$ and $\text{NO}_2^-/\text{NO}_3^-$.

Pairs of substances that can form each other by loss or gain of electrons are called *redox conjugate pairs or couples*.

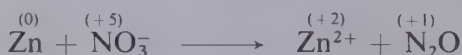
The Oxidation Number Change Method

In this method the oxidation numbers of the atoms that change their oxidation number are identified first and then the total increase in oxidation number is equated to the total decrease in oxidation number by adjusting coefficients. The complete method is outlined in the following example.

- (1) Write down the correct formulas of the reactants and their products.



- (2) Identify and mark in the oxidation numbers of the atoms changing oxidation number.

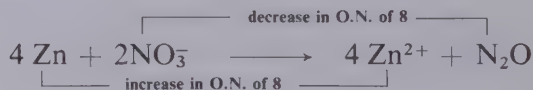


If the number of atoms that are changing their oxidation number is not the same on both sides of the equation, adjust the coefficients in front of the formulas so that they are in fact equal.

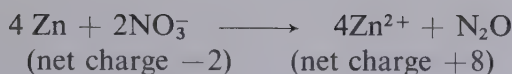


- (3) Calculate the increase and decrease in oxidation number and equate them by adjusting coefficients in front of the reactants and their products.

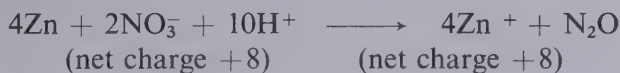
For each nitrogen atom there is a decrease in oxidation number from +5 to +1; so for the two nitrogen atoms the decrease in oxidation number is 8. For each zinc atom there is an increase in oxidation number from 0 to +2; so to have the same change in oxidation number as for the two nitrogen atoms, four zinc atoms are required.



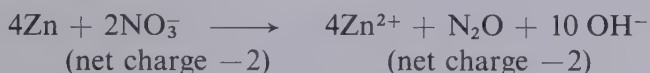
- (4) To complete the balance, the net charge of the reacting particles is made equal to the net charge of the products by adding either H^+ ions to the more negative side or OH^- ions to the least negative side depending on whether the reaction is taking place in acid or alkaline solution.



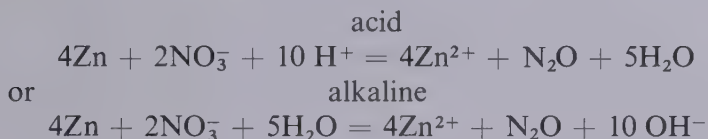
In **acid** solution—addition of H^+ ions



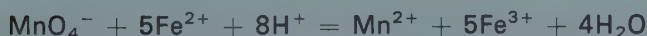
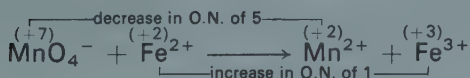
In **alkaline** solution—addition of OH^- ions



- (5) Finally the balance of oxygen atoms is achieved by adding a water molecule (H_2O) for each oxygen atom short, to the side which has least oxygen atoms i.e.



Example



The Half Equation Method

The first requirement in this method is to write down the balanced half equations for the oxidiser and reducer. The procedure for balancing a half equation is summarized by the following steps.

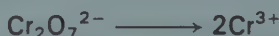
(a) *In Acid Solution*

Example 1

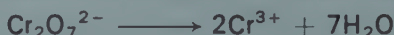
- (1) Write down the formula of the reactant and its known or predicted product.



If necessary, balance the atoms on both sides other than H and O by adjusting coefficients.



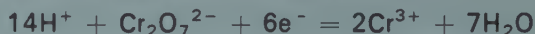
- (2) Add H_2O molecules to the side short of oxygen atoms



- (3) Add H^+ ions to the side short of hydrogen atoms



- (4) Add electrons to the side which has the most positive net charge so that the net charge on both sides is the same.



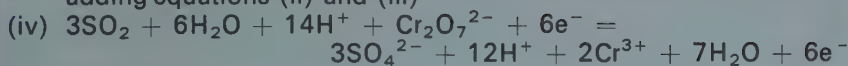
Example 2

- | | |
|--|----------------------|
| (1) $\text{SO}_2 \longrightarrow \text{SO}_4^{2-}$ | (in acid solution) |
| (2) $\text{SO}_2 + 2\text{H}_2\text{O} \rightarrow \text{SO}_4^{2-}$ | (balance O atoms) |
| (3) $\text{SO}_2 + 2\text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 4\text{H}^+$ | (balance H atoms) |
| (4) $\text{SO}_2 + 2\text{H}_2\text{O} = \text{SO}_4^{2-} + 4\text{H}^+ + 2\text{e}^-$ | (balance net charge) |

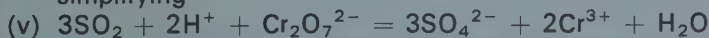
To balance the equation for the reaction between sulphur dioxide and a dichromate ion in an acid solution the half equations for the conjugates $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$ and $\text{SO}_2/\text{SO}_4^{2-}$ must be worked out as shown above. Inspection of these equations reveals that the $\text{Cr}_2\text{O}_7^{2-}$ ion is the electron acceptor or oxidiser while the SO_2 is the electron donor or reducer. In any redox reaction the electrons lost by the reducer must equal the number of electrons gained by the oxidiser. To achieve this the complete half equations must be multiplied throughout by a coefficient so that electrons given up do in fact equal those gained. On adding the left hand sides of the half equations and also the right hand sides and then cancelling common terms one gets the simplest equation, as shown below.

- (i) $\text{SO}_2 + 2\text{H}_2\text{O} = \text{SO}_4^{2-} + 4\text{H}^+ + 2\text{e}^-$
multiply by coefficient 3
- (ii) $3\text{SO}_2 + 6\text{H}_2\text{O} = 3\text{SO}_4^{2-} + 12\text{H}^+ + 6\text{e}^-$
- (iii) $14\text{H}^+ + \text{Cr}_2\text{O}_7^{2-} + 6\text{e}^- = 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$

adding equations (ii) and (iii)



simplifying



(b) In Alkaline Solution

To balance a redox reaction in alkaline solution an additional step is necessary in step 3 of example 1 and example 2, namely the addition of OH^- ions to both sides of the half equation in sufficient numbers to exactly neutralize the H^+ ions to water molecules.

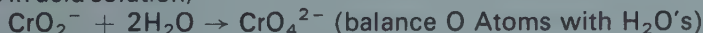
Example 1

Consider the oxidation of the CrO_2^- ion to the CrO_4^{2-} ion in alkaline solution.

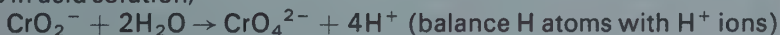
(1) As in acid solution,



(2) As in acid solution,



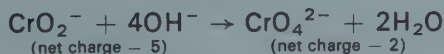
(3) As in acid solution,



Remove H^+ ions from the half equation by adding an equal number of OH^- ions to both sides of the equation.



The H^+ and OH^- ions on the same side are combined as water molecules, and then cancelled with water molecules on the other side.

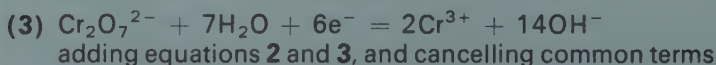
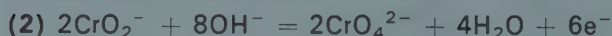
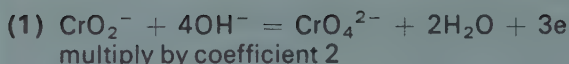


(4) Balance the net charge of the ions on each side by adding electrons to the least negative side.



The balanced equation for the reaction between CrO_2^- and say $Cr_2O_7^{2-}$ ions in alkaline solutions is achieved as in acid solution, by working out the half equations for both ions in alkaline solution and then multiplying throughout by coefficients to make the number of electrons lost equal to the number of electrons gained.

Example 2



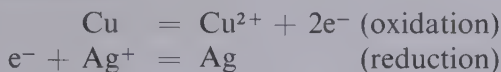
Whichever method you use to balance a redox equation, it is always wise to check that the final equation balances with respect to the number of each atom on both sides and also the net charge of the ions on both sides.

Now that you have learnt to write balanced redox equations it should be pointed out that although it may be possible to write a balanced equation for an oxidiser reacting with a reducer, in practice these substances may show very little tendency to react at all. The extent of a redox reaction, can in fact be predicted with the aid of half reaction potentials and these will be discussed in a later section.

Harnessing the Electron Transfer in Redox Reactions

Place a piece of shiny copper into a solution containing silver nitrate and observe any changes that take place over a period of time. Grey crystals form on the copper reasonably quickly and the colourless solution gradually turns blue. Considering that the reactants are copper atoms (Cu), silver ions (Ag^+), and nitrate ions (NO_3^-) the question is, 'Which one has formed the grey deposit and which one the blue coloration?' From your observation of salts containing the hydrated copper ion Cu^{2+} , such as $\text{Cu}^{2+}\text{SO}_4$ and $\text{Cu}^{2+}(\text{NO}_3)_2$ you have realised that the blue colour is due to the formation of the blue hydrated Cu^{2+} ion and the grey deposit could only be silver.

Consider what has happened invisibly in the solution for this result. For copper atoms to form ions they must have lost electrons and for the silver ions to have formed silver atoms they must have gained electrons.



Scientists during the eighteenth century observed identical electron transfer reactions, but were not aware that electrons were actually flowing in large numbers from the copper atoms to the silver ions in solution.

The first clue to this secret came in 1791 when an Italian anatomist Luigi Galvani (1737-1798) made a chance observation that the muscles in the legs of recently dissected frogs contracted when placed near an electrical discharge. Although at first not interested in the phenomenon, he made another chance observation that made him become involved in the problem. He discovered that this muscular contraction also occurred when freshly dissected frogs were hung to dry on an iron nail in his garden by copper hooks that had been pushed through their spinal cords.



ALESSANDRO VOLTA (1745-1827)

A fellow countryman Alessandro Volta (1745-1827) read Galvani's reports with interest but disputed the belief that the electricity which he had proved necessary for muscular contraction, came from within the animal and was simply discharged on contact with metals. Volta claimed that the contraction was due to a

current of electricity produced by the contact of two different metals separated by a liquid conductor. In 1799 Volta proved his beliefs by constructing his famous *voltaic cell* from a series of silver and zinc discs separated by absorbent materials soaked in water. He built up a battery of such cells, the famous *couronne de tasses* or crown of cups, which apart from being a sensation at the beginning of the nineteenth century, provided the tool for other great discoveries such as electro-magnetism and electro-chemistry.

John Daniell made the next great contribution in 1835, when after years of investigating why voltaic cells rapidly lost their potential to supply electrons, he constructed his well known *Daniell Cell* which gave a constant potential.

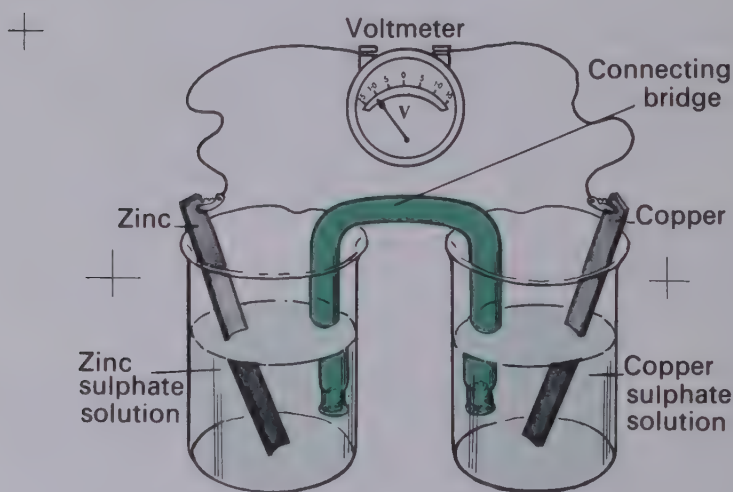


Figure 4. An electrochemical cell (the Daniell Cell). The connecting bridge is an inverted U-tube filled with a saturated solution of potassium chloride and sealed with plugs of cotton-wool

You could easily recreate Daniell's original cell in the laboratory by placing a piece of copper in a beaker of copper sulphate solution, a piece of zinc in a beaker of zinc sulphate solution and then connecting the metals to the terminals of a voltmeter. The solutions are joined electrically by means of a porous medium, called the connecting bridge, such as filter paper soaked in an electrolyte (dilute sulphuric acid).

This cell has all the features of what we now generally call an *electrochemical cell* or a cell which produces electricity as a result of a chemical redox (or electron transfer) reaction. The whole point of dividing the cell into two half cells, namely the electron donor (reducer) half cell and the electron acceptor (oxidiser) half cell is to force the electrons released by the reducer to travel to the oxidiser via an external circuit, rather than through the solution. In your Zn-Cu cell you will notice copper depositing on the copper rod. Can you predict

- (1) the half equations for the reactions occurring in each half cell,
- (2) which way the electrons are *actually* moving in the external circuit,
- (3) which cell is the oxidiser and
- (4) which way the positive and negative ions in the connecting bridge of filter paper will tend to move?

With electrochemical cells and other types of cells, called electrolytic cells which we look at later, the electrode at which a loss of electrons occurs (oxidation) is called the **anode** and the electrode at which a gain of electrons occurs (reduction) is called the **cathode**. Using this definition, which electrode in the Daniell cell is the anode?

You might like to investigate the function of the bridge by seeing what happens if you remove it or replace it with a *dry* filter paper or a filter paper soaked in a *molecular liquid* such as benzene, carbon tetrachloride or methylene chloride. Why will electrons tend to be repelled away from the copper electrode, and the current stop, unless positive ions alone enter the copper half cell and replace the positive Cu^{2+} ions that are deposited?

Standard Half Cells or Electrodes

Half cells used in the laboratory are constructed in order to meet certain requirements and are therefore called *standard half cells*.

A Standard Metallic Half Cell

This consists of a piece of pure metal standing in a solution which is one molar (1M) with respect to its ion. For example a piece of pure metallic zinc in a one molar solution of zinc

nitrate, is given the symbol Zn/Zn^{2+} ; other examples are Cu/Cu^{2+} , Mg/Mg^{2+} .

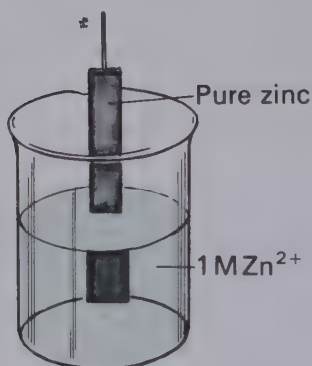


Figure 5. A standard zinc half-cell. A piece of pure zinc is placed in a molar solution of a Zn^{2+} salt, such as $\text{Zn}(\text{NO}_3)_2$ at 25°C

A Standard Solution Half Cell

This consists of an inert electrode (e.g. Pt) standing in a solution which is 1M with respect to an oxidising or reducing ion and 1M with respect to its conjugate ion, e.g. $\text{MnO}_4^-/\text{Mn}^{2+}$, $\text{Fe}^{2+}/\text{Fe}^{3+}$, $\text{Sn}^{2+}/\text{Sn}^{4+}$.

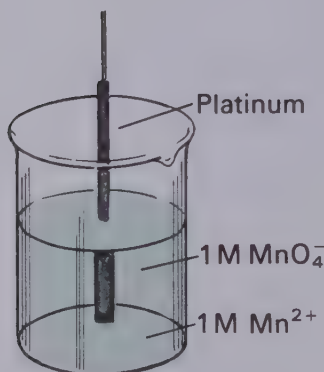


Figure 6. A standard $\text{MnO}_4^-/\text{Mn}^{2+}$ half-cell. A platinum electrode is placed in a solution containing a mixture of one molar MnO_4^- salt, such as KMnO_4 , and one molar Mn^{2+} , such as MnSO_4

A Standard Gaseous Half Cell

This consists of a gas at one atmosphere pressure bubbling over finely divided platinum on a platinum electrode immersed in a solution which is 1M with respect to the ions of the gas, e.g. Cl_2/Cl^- , H_2/H^+ .

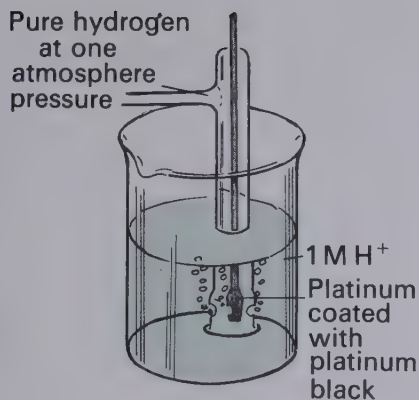


Figure 7. Standard hydrogen half-cell. Pure hydrogen gas at a pressure of one atmosphere is passed over platinum coated with specially prepared platinum (called platinum black), immersed in a one molar solution of H^+ such as HCl

All half cells show either a positive or negative potential to lose electrons. As yet there has not been any satisfactory method devised to measure this potential for a single half cell in isolation by itself. How then do we measure electrode potentials?

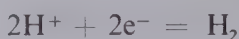
Standard Electrode Potentials

Before Volta constructed his famous cell, he performed many experiments with different pairs of metals by touching them on his tongue with the other ends in contact. In this way he detected differences which led him to a list or series which we could call an electrochemical series or activity series, that gave the relative tendency of metals to give up electrons. It was not by accident that Volta connected zinc and silver discs together, as you will appreciate when you know the relative tendencies of these metals to lose electrons.

You can repeat similar experiments to those of Volta, by placing different metals in solutions containing ions of other metals. After noting whether there is a reaction or not you can get a *relative* idea of the *tendency or potential* of a metal to give up electrons compared with other metals. To measure this potential accurately as a voltage, we have to set up a standard half cell or

electrode for the metal, and then connect it to another half cell which acts as a reference electrode. The standard hydrogen electrode whose details are shown in figure 7 is the accepted standard.

At this electrode, two reactions are possible:



and



Actually both of these reactions exist in a dynamic equilibrium with each other in solution at the electrode i.e. $2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2$. This means that hydrogen molecules are continually losing electrons and forming hydrogen ions, and hydrogen ions are continually gaining these electrons and reforming hydrogen molecules.

By *definition* the potential of hydrogen ions to be reduced to hydrogen molecules or hydrogen molecules to be oxidised to hydrogen ions is taken as being *zero*. Hence the standard electrode potential for a hydrogen cell $E^\circ(\text{H}_2/\text{H}^+)$ is defined as 0.00 volts in a one molar (1M) solution at 25°C. It does not mean that this particular half cell actually has zero potential, but only that it can be used to establish a relative scale of individual half cell

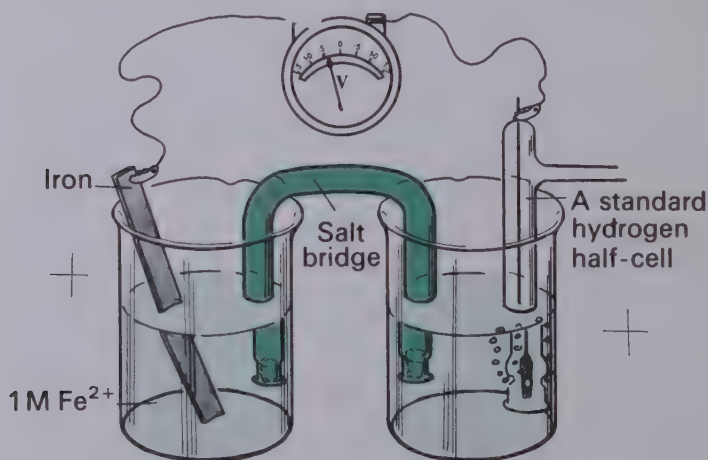
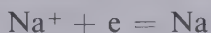


Figure 8. The measurement of the standard electrode potential of a Fe/Fe^{2+} half-cell using the standard hydrogen half-cell connected by a saturated solution of potassium chloride in the salt bridge

potentials. Zero volts is a convenient standard, because, to measure the **Standard Electrode Potential** (E°) of another electrode, this electrode is simply bridged to a standard hydrogen electrode (see figure 8) and the potential difference measured. This potential difference is called the standard electrode potential of the electrode being measured.

Standard Electrode Potentials are quoted as **Oxidation Potentials** (the potential of the electrode to lose electrons) or as **Reduction Potentials** (the potential of the electrode to gain electrons) both compared with the standard hydrogen electrode. The potential of an electrode to gain electrons will of course be equal numerically, but opposite in sign, to its potential to lose them. The Standard Electrode Potential (E°) for the Na/Na^+ reaction can be expressed in two ways.

The Standard **Reduction** Potential for the reaction



is -2.71 volt.

This can be written $E^\circ (\text{Na}^+/\text{Na}) = -2.71$ volt.

The Standard **Oxidation** Potential for the reaction



is $+2.71$ volt.

This can be written $E^\circ (\text{Na}/\text{Na}^+) = +2.71$ volt.

The actual measurement of the electrode potential for the Fe/Fe^{2+} electrode can be carried out as shown in figure 8.

If the voltage of this cell is 0.44 volt what does this tell you about the value of the E° for the standard Fe/Fe^{2+} half cell? Electrons actually flow towards the standard hydrogen half cell in this cell. What does this suggest about the sign (positive or negative) of the potential of the Fe/Fe^{2+} half cell to lose electrons compared with the standard hydrogen electrode?

Many of the E° values quoted in the table of Standard Electrode Potentials were calculated experimentally by connecting the various standard metal, solution, or gaseous half cells, to a standard hydrogen electrode and then recording the overall potential and the direction of the electron flow so as to give E° a sign.

Standard Oxidation Potentials for Half Reactions Ionic Concentrations, 1 M in Water at 25° C

All ions are in water

Strength as Reducing Agent	HALF REACTION	E° (volt)	Strength as Oxidising Agent
Very strong reducing agents	$\text{Li} \longrightarrow \text{e}^- + \text{Li}^+$	+3.00	Very weak oxidising agents
	$\text{Rb} \longrightarrow \text{e}^- + \text{Rb}^+$	+2.92	
	$\text{K} \longrightarrow \text{e}^- + \text{K}^+$	+2.92	
	$\text{Cs} \longrightarrow \text{e}^- + \text{Cs}^+$	+2.92	
	$\text{Ba} \longrightarrow 2\text{e}^- + \text{Ba}^{2+}$	+2.90	
	$\text{Sr} \longrightarrow 2\text{e}^- + \text{Sr}^{2+}$	+2.89	
	$\text{Ca} \longrightarrow 2\text{e}^- + \text{Ca}^{2+}$	+2.87	
	$\text{Na} \longrightarrow \text{e}^- + \text{Na}^+$	+2.71	
	$\text{Mg} \longrightarrow 2\text{e}^- + \text{Mg}^{2+}$	+2.37	
	$\text{Al} \longrightarrow 3\text{e}^- + \text{Al}^{3+}$	+1.66	
Reducing strength increases ↑	$\text{Mn} \longrightarrow 2\text{e}^- + \text{Mn}^{2+}$	+1.18	Oxidising strength increases ↓
	$\text{H}_{2(\text{g})} + 2\text{OH}^- \longrightarrow 2\text{e}^- + 2\text{H}_2\text{O}$	+0.83	
	$\text{Zn} \longrightarrow 2\text{e}^- + \text{Zn}^{2+}$	+0.76	
	$\text{Cr} \longrightarrow 3\text{e}^- + \text{Cr}^{3+}$	+0.74	
	$\text{H}_2\text{Te} \longrightarrow 2\text{e}^- + \frac{1}{8}\text{Te}_8 + 2\text{H}^+$	+0.72	
	$2\text{Ag} + \text{S}^{2-} \longrightarrow 2\text{e}^- + \text{Ag}_2\text{S}$	+0.69	
	$\text{Fe} \longrightarrow 2\text{e}^- + \text{Fe}^{2+}$	+0.44	
	$\text{H}_{2(\text{g})} \longrightarrow 2\text{e}^- + 2\text{H}^+ (10^{-7}\text{M})$	+0.42	
	$\text{Cr}^{2+} \longrightarrow \text{e}^- + \text{Cr}^{3+}$	+0.41	
	$\text{H}_2\text{Se} \longrightarrow 2\text{e}^- + \frac{1}{8}\text{Se}_8 + 2\text{H}^+$	+0.40	
	$\text{Co} \longrightarrow 2\text{e}^- + \text{Co}^{2+}$	+0.28	
	$\text{Ni} \longrightarrow 2\text{e}^- + \text{Ni}^{2+}$	+0.25	
	$\text{Sn} \longrightarrow 2\text{e}^- + \text{Sn}^{2+}$	+0.14	
	$\text{Pb} \longrightarrow 2\text{e}^- + \text{Pb}^{2+}$	+0.13	
	$\text{H}_{2(\text{g})} \longrightarrow 2\text{e}^- + 2\text{H}^+$	0.00	
	$\text{H}_2\text{S}_{(\text{g})} \longrightarrow 2\text{e}^- + \frac{1}{8}\text{S}_8 + 2\text{H}^+$	-0.14	
	$\text{Sn}^{2+} \longrightarrow 2\text{e}^- + \text{Sn}^{4+}$	-0.15	
	$\text{Cu}^+ \longrightarrow \text{e}^- + \text{Cu}^{2+}$	-0.15	
	$\text{SO}_{2(\text{g})} + 2\text{H}_2\text{O} \longrightarrow 2\text{e}^- + \text{SO}_4^{2-} + 4\text{H}^+$	-0.17	
	$\text{Cu} \longrightarrow 2\text{e}^- + \text{Cu}^{2+}$	-0.34	
	$\text{Cu} \longrightarrow \text{e}^- + \text{Cu}^+$	-0.52	
	$2\text{I}^- \longrightarrow 2\text{e}^- + \text{I}_2$	-0.53	
	$\text{H}_2\text{O}_2 \longrightarrow 2\text{e}^- + \text{O}_{2(\text{g})} + 2\text{H}^+$	-0.68	
	$\text{Fe}^{2+} \longrightarrow \text{e}^- + \text{Fe}^{3+}$	-0.77	
	$\text{NO}_{2(\text{g})} + \text{H}_2\text{O} \longrightarrow \text{e}^- + \text{NO}_3^- + 2\text{H}^+$	-0.78	
	$\text{Hg}_{(\text{l})} \longrightarrow 2\text{e}^- + \text{Hg}^{2+}$	-0.78	
	$\text{Hg}_{(\text{l})} \longrightarrow \text{e}^- + \frac{1}{2}\text{Hg}_2^{2+}$	-0.79	
	$\text{Ag} \longrightarrow \text{e}^- + \text{Ag}^+$	-0.80	
	$\text{H}_2\text{O} \longrightarrow 2\text{e}^- + \frac{1}{2}\text{O}_{2(\text{g})} + 2\text{H}^+ (10^{-7}\text{M})$	-0.82	
	$\text{NO}_{(\text{g})} + 2\text{H}_2\text{O} \longrightarrow 3\text{e}^- + \text{NO}_3^- + 4\text{H}^+$	-0.96	
	$\text{Au} + 4\text{Cl}^- \longrightarrow 3\text{e}^- + \text{AuCl}_4^-$	-1.00	
	$2\text{Br}^- \longrightarrow 2\text{e}^- + \text{Br}_{2(\text{l})}$	-1.06	
	$\text{H}_2\text{O} \longrightarrow 2\text{e}^- + \frac{1}{2}\text{O}_{2(\text{g})} + 2\text{H}^+$	-1.23	
	$\text{Mn}^{2+} + 2\text{H}_2\text{O} \longrightarrow 2\text{e}^- + \text{MnO}_2 + 4\text{H}^+$	-1.28	
	$2\text{Cr}^{3+} + 7\text{H}_2\text{O} \longrightarrow 6\text{e}^- + \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+$	-1.33	
	$2\text{Cl}^- \longrightarrow 2\text{e}^- + \text{Cl}_{2(\text{g})}$	-1.36	
	$\text{Au} \longrightarrow 3\text{e}^- + \text{Au}^{3+}$	-1.50	
	$\text{Mn}^{2+} + 4\text{H}_2\text{O} \longrightarrow 5\text{e}^- + \text{MnO}_4^- + 8\text{H}^+$	-1.52	
	$2\text{H}_2\text{O} \longrightarrow 2\text{e}^- + \text{H}_2\text{O}_2 + 2\text{H}^+$	-1.77	
	$2\text{F}^- \longrightarrow 2\text{e}^- + \text{F}_{2(\text{g})}$	-2.87	
Very weak reducing agents			Very strong oxidising agents

Standard Reduction Potentials for Half Reactions Ionic Concentrations, 1 M in Water at 25° C

All ions are in water

Strength as Oxidising Agent	HALF REACTION	E° (volt)	Strength as Reducing Agent
Very strong oxidising agents	$F_{2(g)} + 2e^- \longrightarrow 2F^-$	+2.87	Very weak reducing agents
	$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$	+1.77	
	$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	+1.52	
	$Au^{3+} + 3e^- \longrightarrow Au$	+1.50	
	$Cl_{2(g)} + 2e^- \longrightarrow 2Cl^-$	+1.36	
	$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$	+1.33	
	$MnO_{2(s)} + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O$	+1.28	
	$\frac{1}{2}O_{2(g)} + 2H^+ + 2e^- \longrightarrow H_2O$	+1.23	
	$Br_{2(l)} + 2e^- \longrightarrow 2Br^-$	+1.06	
	$AuCl_4^- + 3e^- \longrightarrow Au + 4Cl^-$	+1.00	
	$NO_3^- + 4H^+ + 3e^- \longrightarrow NO_{(g)} + 2H_2O$	+0.96	
	$\frac{1}{2}O_{2(g)} + 2H^+ (10^{-7}M) + 2e^- \longrightarrow H_2O$	+0.82	
	$Ag^+ + e^- \longrightarrow Ag$	+0.80	
	$\frac{1}{2}Hg_2^{2+} + e^- \longrightarrow Hg_{(l)}$	+0.79	
	$Hg^{2+} + 2e^- \longrightarrow Hg_{(l)}$	+0.78	
	$NO_3^- + 2H^+ + e^- \longrightarrow NO_{2(g)} + H_2O$	+0.78	
	$Fe^{3+} + e^- \longrightarrow Fe^{2+}$	+0.77	
	$O_{2(g)} + 2H^+ + 2e^- \longrightarrow H_2O_2$	+0.68	
	$I_{2(s)} + 2e^- \longrightarrow 2I^-$	+0.53	
	$Cu^+ + e^- \longrightarrow Cu$	+0.52	
	$Cu^{2+} + 2e^- \longrightarrow Cu$	+0.34	
	$SO_4^{2-} + 4H^+ + 2e^- \longrightarrow SO_{2(g)} + 2H_2O$	+0.17	
	$Cu^{2+} + e^- \longrightarrow Cu^+$	+0.15	
	$Sn^{4+} + 2e^- \longrightarrow Sn^{2+}$	+0.15	
	$S + 2H^+ + 2e^- \longrightarrow H_2S_{(g)}$	+0.14	
	$2H^+ + 2e^- \longrightarrow H_{2(g)}$	0.00	
	$Pb^{2+} + 2e^- \longrightarrow Pb$	-0.13	
	$Sn^{2+} + 2e^- \longrightarrow Sn$	-0.14	
	$Ni^{2+} + 2e^- \longrightarrow Ni$	-0.25	
	$Co^{2+} + 2e^- \longrightarrow Co$	-0.28	
	$Se + 2H^+ + 2e^- \longrightarrow H_2Se_{(g)}$	-0.40	
	$Cr^{3+} + e^- \longrightarrow Cr^{2+}$	-0.41	
	$2H^+ (10^{-7}M) + 2e^- \longrightarrow H_{2(g)}$	-0.41	
	$Fe^{2+} + 2e^- \longrightarrow Fe$	-0.44	
	$Ag_2S + 2e^- \longrightarrow 2Ag + S^{2-}$	-0.69	
	$Te + 2H^+ + 2e^- \longrightarrow H_2Te_{(g)}$	-0.72	
	$Cr^{3+} + 2e^- \longrightarrow Cr$	-0.74	
	$Zn^{2+} + 2e^- \longrightarrow Zn$	-0.76	
	$2H_2O + 2e^- \longrightarrow 2OH^- + H_{2(g)}$	-0.83	
	$Mn^{2+} + 2e^- \longrightarrow Mn$	-1.18	
	$Al^{3+} + 3e^- \longrightarrow Al$	-1.66	
	$Mg^{2+} + 2e^- \longrightarrow Mg$	-2.37	
	$Na^+ + e^- \longrightarrow Na$	-2.71	
	$Ca^{2+} + 2e^- \longrightarrow Ca$	-2.87	
	$Sr^{2+} + 2e^- \longrightarrow Sr$	-2.89	
	$Ba^{2+} + 2e^- \longrightarrow Ba$	-2.90	
	$Cs^+ + e^- \longrightarrow Cs$	-2.92	
Very weak oxidising agents	$K^+ + e^- \longrightarrow K$	-2.92	Very strong reducing agents
	$Rb^+ + e^- \longrightarrow Rb$	-2.92	
	$Li^+ + e^- \longrightarrow Li$	-3.00	

Oxidising strength increases

Reducing strength increases

You may be interested to read how the E° 's of half cells such as the Na/Na^+ and the F_2/F^- are measured. As elements such as sodium and fluorine react with water, these elements are not placed in solutions containing their ions but rather in a combination of specially constructed cells.

It can be shown experimentally that the electrode potential E° for a half cell varies with changes in temperature, and also with changes in the concentration of the ionic species or the pressure of any gaseous species. Consequently, the measurement of the Standard Electrode Potential has to be carried out under exact conditions.

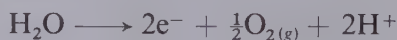
The values of the *Standard Electrode Potentials* E° (the superscript zero means standard state) quoted in the following tables, assume that:

- (i) the *temperature* of the solutions is 25°C ,
- (ii) the effective *concentrations* of the ionic species in solution are *one molar*, and
- (iii) the effective *partial pressures* of any gaseous species is *one atmosphere* pressure (760 mm Hg).

Two tables are given. The first is a Table of Standard Oxidation Potentials in which there is an increase in oxidising strength from very weak oxidising agents to very strong oxidising agents. The second is a Table of Standard Reduction Potentials in which there is an increase in reducing strength from very weak reducing agents to very strong reducing agents.

In the table of Standard Oxidation Potentials it is stated quite clearly that the E° values are given for half reactions with ionic concentrations of 1M in water. These potentials are measured when the cell is operating essentially reversibly and therefore reflect equilibrium conditions at the electrodes. In general, the higher the concentration of ions in solution, the greater will be the speed of rejoining the electrode, and therefore the smaller the tendency for the electrode reaction to occur. The electrode oxidation potential (E) is therefore somewhat lower when the concentration of ions is higher, and vice versa for the electrode reduction potential.

As an example of the variation of E with concentration, consider the half reaction



When the concentration of H^+ (expressed $[\text{H}^+]$) is 10^{-14} mole litre $^{-1}$, ($\text{pH} = 14$), the oxidation potential is -0.40 volt.

When the $[\text{H}^+]$ is 10^{-7} mole litre $^{-1}$ ($\text{pH} = 7$), oxidation potential is -0.82 volt.

When the $[\text{H}^+]$ is 10^{-0} mole litre $^{-1}$ ($\text{pH} = 0$), oxidation potential is -1.23 volt.

The variation of electrode potential with changing concentrations of the hydrogen ion has an important application in the measurement of the pH of a solution. Instead of using an indicator, one can use a hydrogen electrode, making the solution in question the other half cell by inserting a platinum electrode and connecting the two by a salt bridge. Since the potential of the standard hydrogen electrode depends on the concentration of hydrogen ion being one molar, if the solution has a different $[\text{H}^+]$, the cell potential is measurable, and the pH ($-\log_{10} [\text{H}^+]$) can be calculated from it. A more detailed account of the measurement of the pH of a solution is discussed in the NSCM booklet, C12 Acids and Bases.

The Use of Standard Electrode Potentials

The Relative Strengths of Oxidants and Reductants

From the tables of E° values given, it can be seen in the Standard Oxidation Potentials table that lithium atoms are the strongest reductant as they show the most positive potential to lose electrons. Conversely in the Standard Reduction Potentials table the lithium ions show the most negative tendency or potential to gain electrons and hence represent the weakest oxidant. This reciprocal or conjugate relationship between oxidisers and reducers is similar to that between acids and their bases. At the other end of the table, fluoride ions are the weakest reducers but fluorine molecules are the strongest oxidiser with a potential of $+2.87$ volt to gain electrons.

What can you say about the potential of zinc and iron to lose electrons and hence can you suggest why pieces of zinc are attached to the steel hulls of ships to prevent rusting or oxidation of the iron?



Figure 9. Photograph of the hull of a ship while it is in the dry dock showing zinc anode blocks used to prevent corrosion of the steel hull by sea-water.

To Predict the Likelihood of a Reaction between an Oxidiser and a Reducer

Consider the situations shown in figure 10.

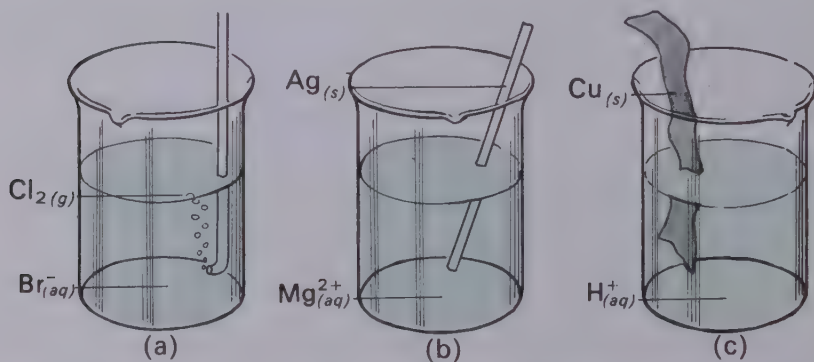


Figure 10. (a) Chlorine gas bubbling through a potassium bromide solution
 (b) Silver rod standing in a magnesium sulphate solution
 (c) Copper sheet standing in an acid solution such as hydrochloric acid

Will a reaction occur in each case? To answer this question, you will have to write down the equations for the two half reactions that could occur in each case and also the E° for these reactions. Before you add half equations to give the equation for the complete reaction you have to make sure that the number of electrons lost equals the number of electrons gained. Even though this may necessitate you multiplying a half equation throughout by a coefficient, the E° value remains the same. This is reasonable as the potential or possibility of say one Br^- ion losing an electron is the same as the potential of two Br^- ions losing two electrons.

Just as the overall equation is calculated by adding the half equations, the overall potential is found by adding the E° 's for these half equations. If the overall potential is positive then the forward reaction is likely, but if it is negative then the back reaction is more likely. What does this last statement suggest about the nature of redox reactions?

The answers to the systems in figure 10 are calculated as follows.

(a) From the Table of Standard Reduction Potentials



From the Table of Standard Oxidation Potentials



Adding the two half equations



The overall potential (E_{total}) for this reaction is obtained by the addition of $E^\circ (\text{Cl}/\text{Cl}^-)$ with $E^\circ (\text{Br}^-/\text{Br})$

$$\text{that is } (+1.36) \text{ volt} + (-1.06) \text{ volt, } = +0.30 \text{ volt.}$$

Since E_{total} is $+0.30$ volt, the reduction of chlorine gas, and oxidation of the bromide ion to bromine liquid is possible. If chlorine gas is bubbled through a potassium bromide (KBr) solution, the colourless solution rapidly turns a red colour because of the oxidation of the bromide ion to bromine.

(b) From the Table of Standard Reduction Potentials



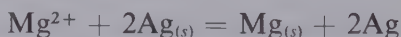
From the Table of Standard Oxidation Potentials



Multiply this oxidation half equation by 2 so as to have the same number of electrons involved in the oxidation half-reaction as with the reduction half-reaction.



Adding the two half-reactions



The overall potential (E_{total}) for this reaction is

$$\begin{aligned} E_{\text{total}} &= E^\circ (\text{Mg}^{2+}/\text{Mg}) + E^\circ (\text{Ag}/\text{Ag}^+) \\ &= (-2.37) \text{ volt} + (-0.80) \text{ volt} \\ &= -3.17 \text{ volt} \end{aligned}$$

The significance of the negative voltage (-3.17 volt) is that equilibrium in the reaction favours the reactants, not the products. Another way of looking at the negative voltage is that the potential of silver atoms to form silver ions is less than the potential of magnesium atoms to form magnesium ions, and hence silver ions will not form in this reaction at the expense of magnesium ions. Silver will not be oxidised to an appreciable extent in a solution of magnesium sulphate.

- (c) This is left as an exercise for you to determine if any reaction is likely when pure copper is placed in a dilute acid solution.

To Predict the E.M.F. of a Cell

Consider the E.M.F. of a $\text{Fe}/\text{Fe}^{2+}-\text{Ag}^+/\text{Ag}$ cell.

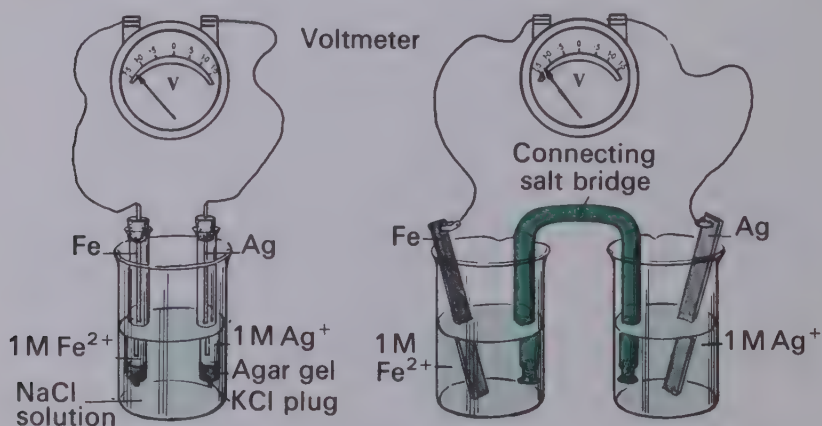


Figure 11. Two arrangements of a $\text{Fe}/\text{Fe}^{2+}-\text{Ag}/\text{Ag}^+$ cell. What voltage will the cell produce?

The $\text{Fe}/\text{Fe}^{2+}-\text{Ag}^+/\text{Ag}$ cell may be constructed in either of the two methods shown. The ionic concentrations in each half cell is 1M, and experimentally the voltage is found to be 1.3 volt.

This cell involves the following two half-reactions:

(i) the reduction half-reaction

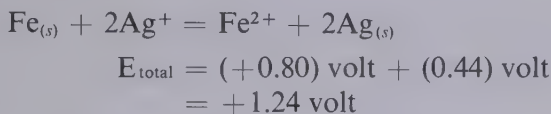


(ii) the oxidation half-reaction



To write a balanced equation for the overall reaction in the cell we have to make the number of electrons lost equal to the number of electrons gained by doubling the half-reaction (i). As previously pointed out we do not double the E° value, as the potential or possibility of one ion to gain one electron is the same as the potential of two ions to gain two electrons.

Adding the two half-reactions



The experimental result of 1.3 volt is in close agreement with the calculated result of 1.24 volt.

Do you think this cell will go on producing 1.24 volt for several weeks? Cells of this type are called *primary cells* and they have the limitation that they cannot be recharged by the reversal of electrical current through the cell. The oxidiser and reducer eventually become exhausted and then they have to be replaced if the cell is to continue to be used. You know from experience that the dry cells that you use in your transistor radios or flash-lights have to be replaced periodically because they are primary cells.

If you cut down the middle of a flashlight cell you should be able to identify most of the substances indicated in figure 12. Try to identify the reducer, the oxidiser, the bridge material and its electrolyte and also suggest possible reactions that occur in each half cell.

Another cell of great commercial importance is the lead storage battery or accumulator that supplies electricity to the electrical circuits in your car. This is an example of a *secondary cell* and differs from a primary cell in that, by reversing the current through

the cell (by means of the generator in a car or by a battery charger) the chemical reaction can be reversed and the oxidiser and reducer returned to their previous state.

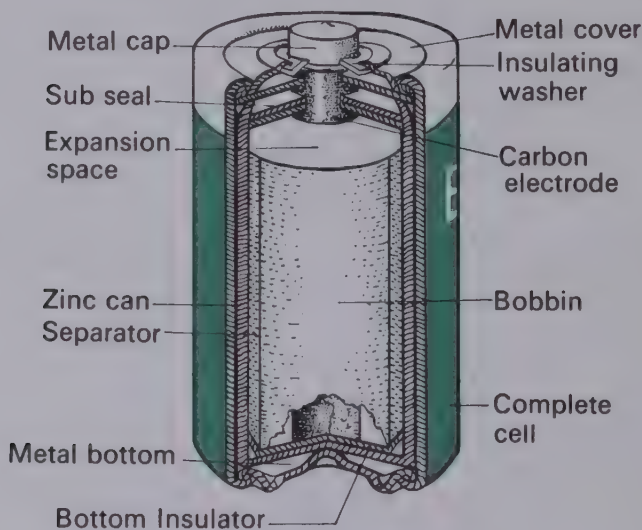
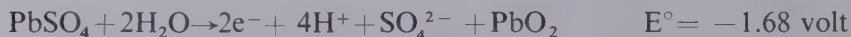


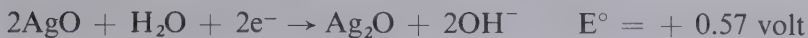
Figure 12. Standard round carbon-zinc primary cell. It has a zinc anode, a carbon cathode and an electrolyte consisting of a moist paste of ammonium chloride (NH_4Cl), zinc chloride (ZnCl_2), manganese dioxide (MnO_2) and carbon particles, which improve conductivity and assist the depolarizing action of the manganese dioxide. The nominal voltage of this type of cell is 1.5 volt

The following half-reactions will be useful for the discussion of the lead storage battery.



By reading about other primary and secondary cells that you may use you will appreciate the way in which scientists have gradually sought more efficient combinations of oxidisers and reducers for use in chemical cells.

The AgO—Cd cell has been used in satellites. This cell can produce a large supply of electrical power and yet it can be made quite small. The electrolyte solution contains KOH, and the equations for the half-reactions are



Miniature batteries are used in watches, movie cameras, and hearing aids to give self-contained power. Miniature batteries have also been used in pacemakers that can be implanted in the human chest for heart stimulation over long periods of time. These batteries often are made of HgO—Zn or Ag₂O—Zn.

Electrolysis

On 30 April 1800 two English scientists Nicholson and Carlisle were experimenting with the newly invented battery of Volta. They were testing the conductivity of various substances by touching them with the ends of two gold wires they had connected to the terminals of the voltaic cell. Quite by accident, they tested the conductivity of water and much to their surprise they observed bubbles of gas coming off from the gold wires immersed in the water. They tested the gases and proved that one of the gases was hydrogen and the other oxygen. To see if metals other than gold could be used as the conducting wires, the scientists used iron and then copper wires and found much to their amazement that in each case only hydrogen came off, and then from only one of the wires. After reading this section you may be able to use your tables of Standard Electrode Potentials to explain this result that could not be explained at the time of the discovery.

The decomposition of an 'ionic' electrolyte into its constituent elements using electricity is called electrolysis. This term was one of several coined by the great English scientist Michael Faraday, who in 1832 discovered and developed most of the fundamental laws and phenomena associated with *electrolytic cells* as we know them today. He used the word **electrolyte** to describe any solution or molten mass that would conduct electricity, the word **ion** to describe the charged particles that existed in these electrolytes and that carried the current, and he used the terms *anode* and *cathode* to describe the positive and negative *electrodes* where the ions lose their charged nature.

Faraday made an incorrect assumption that the molecules of an electrolyte are actually decomposed by the electric current into

positive and negative ions. In 1886 the Swedish physicist Svante Arrhenius put forward the revolutionary idea of *electrolytic dissociation*, namely that some of the *molecules* of an electrolyte when dissolved in water break up spontaneously into ions of opposite charge. Arrhenius also correctly predicted that the electrons move through solutions attached to the negative ions, in fact, the current is the moving ions, and further that the ions on reaching the electrode of opposite charge have their charges neutralized, with the result that uncharged atoms or molecules are deposited.

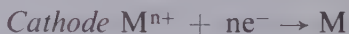


MICHAEL FARADAY (1791-1867)

Actually the *negative ions* move to the positive anode (hence they are called *anions*) where they lose their negative charge by transferring electrons to the anode.



The *positive ions* migrate to the negative cathode (hence they are called *cations*) where they gain the electrons 'pumped' around from the anode by the battery.



From this description what *type* of reaction occurs at the electrodes during electrolysis?

After the discovery by Nicholson and Carlisle in 1800 that

liquid water decomposed when electrolyzed, little progress was made with the electrolysis of other substances until scientists realised that ionic solids or polar molecular substances would not conduct electricity until they were either dissolved in water or melted. Do you know the reason for this requirement?

One of the first men to lead the breakthrough was Sir Humphry Davy born in 1778, the son of a wood carver. On 6 October 1807 he was passing an electric current through *fused* potassium hydroxide when he suddenly saw the first tiny globules of molten potassium break through the surface and take fire. So excited was he at his discovery, that he danced around the room in ecstasy. A few days later he made sodium from fused sodium hydroxide and then followed the electrolysis of a wide range of solutions and melts.

In Davy's experiment the only ions present were potassium ions (K^+) and the hydroxide ions (OH^-) which moved to the electrodes of opposite charge. The K^+ ions moved to the negative cathode where they *gained* electrons and were *reduced* to potassium atoms.

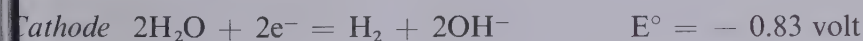


At the anode the OH^- ions gave up their electrons to the electrode which were then forced around the external circuit to the cathode by the battery. Can you work out what product the OH^- ions formed when they were oxidised?

Electrolysis of Aqueous Solutions

Try passing an electric current through distilled water using platinum or carbon electrodes connected to a 6 or 12 volt *direct current* supply.

From visual observation it appears that there is no electrolysis effect at either electrode. Actually there is very slight electrical conductivity and hence decomposition at the electrodes but this can only be detected with the aid of sensitive meters to measure the slight current that flows. At each electrode the polar water molecules orientate themselves as shown in figure 13, and seeing that they are the only species present, they attempt to be oxidised at the anode and reduced at the cathode according to the half reactions shown below.





From these values of E° you might expect that pure water should be oxidised and reduced reasonably easily using moderate voltages.

In practice pure water tends to resist electrolysis but when positive and negative ions are added, it is oxidised and reduced at the electrodes very easily.

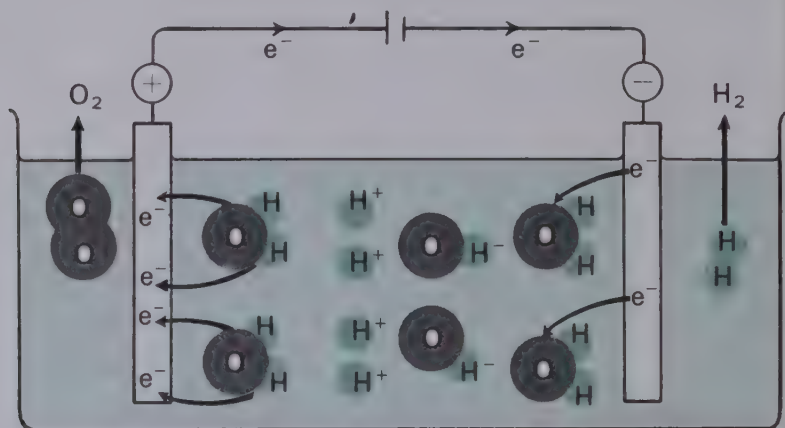


Figure 13. The electrolysis of water showing the orientation and decomposition at the electrodes

Look at figure 14 and predict what effect the *negative* hydroxide (OH^-) produced at the cathode will have on *negative* electrons approaching from the anode. Then consider what effect *positive* sodium ions (Na^+) released from say Na^+Cl^- added to the water will have on these OH^- ions crowded around the cathode. Actually both the H^+ and OH^- ions produced at the electrodes tend to create a potential in opposition to the applied voltage. When positive and negative ions are added, such as Na^+ and Cl^- they will *attract* away the OH^- and H^+ ions respectively and hence remove this back electromotive force that they create.

Once you have added some sodium chloride to water and have proved that oxygen and hydrogen are released readily, try the following variations, observe the results and try to explain what you see.

- (1) Use an anode made of iron or copper and explain why oxygen is no longer liberated.

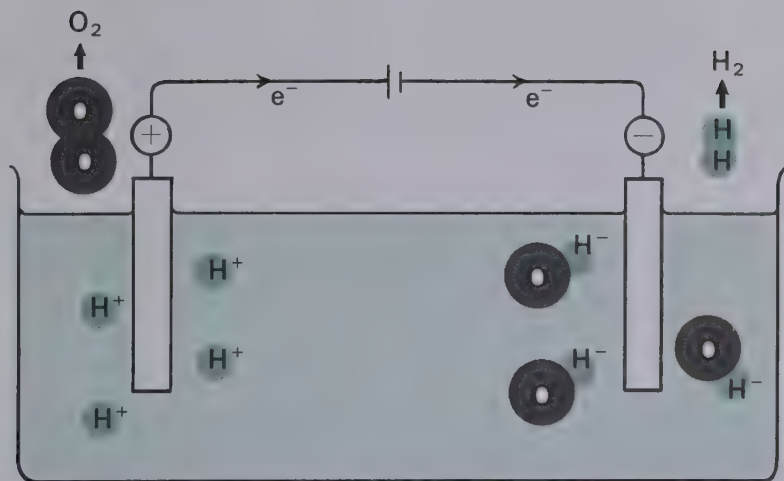


Figure 14. What effect will the H^+ ions and OH^- ions produced during the electrolysis of water have on the movement of electrons in the external circuit?

- (2) Use 6 volts alternating current and explain why the products are impure.
 - (3) Add excess sodium chloride to the solution and consider why chlorine rather than oxygen is liberated at the anode.
- To help you answer these questions consider the electrolysis of the following aqueous solutions.

(a) Dilute Sodium Chloride Solution (Inert electrodes)

In solution there are Na^+ and Cl^- ions and H_2O molecules. At the anode Cl^- ions and H_2O molecules are the only two species present. Their possible electrode reactions are



Because H_2O molecules show the less negative or more positive potential to lose electrons, oxygen gas is evolved and the solution around the electrode becomes acidic.

At the *cathode* Na^+ ions and H_2O molecules are present and their potential electrode reactions are



Once again water molecules show the more positive potential

to gain electrons and therefore hydrogen gas forms and the solution around the cathode becomes basic. Like any redox reaction the electrons being lost must equal the number gained, otherwise a surplus of electrons would develop. To indicate this, the cathode equation is better represented as

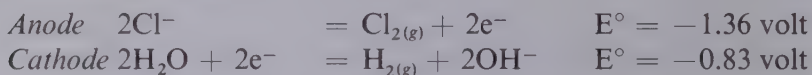


which suggests that two volumes of hydrogen should form for every one volume of oxygen as is the case in practice.

(b) Concentrated Sodium Chloride Solution (*Inert Electrodes*)

At the *anode* chlorine is released rather than oxygen as in dilute solution. When the Cl^- ion is in high concentration the potential for Cl^- ions to lose electrons must become more positive (or less negative) than the potential for H_2O molecules to lose electrons. The E° for Cl^-/Cl_2 must become less negative than -1.23 volt.

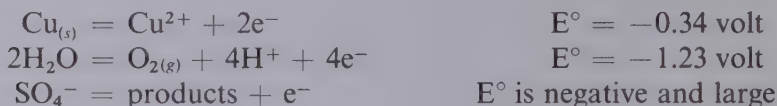
At the cathode the same reaction occurs as in dilute solution which indicates that even in high concentration the E° of Na^+/Na does not become more positive than -0.83 volt. The electrode reactions then are



As the electrons lost do equal the electrons gained, the half equations indicate that equal volumes (or moles) of hydrogen and chlorine will be liberated.

(c) Copper Sulphate Solution (*Copper Electrodes*)

At the *anode* there will be *three* species present which can potentially lose electrons according to the half equations

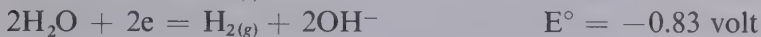
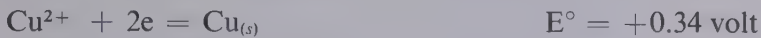


The preferred electrode reaction is



and hence these Cu^{2+} ions formed join those already in solution from the copper sulphate solution.

At the cathode Cu^{2+} ions and H_2O molecules are present, both of which can potentially gain electrons.



The Cu^{2+} ions show the more positive potential to gain electrons and are hence deposited on the cathode. Essentially copper atoms are being torn away from the anode and are being transported through the solution and deposited on the cathode. This process is of industrial importance in Australia in the refining of copper.



Figure 15. Hanging from the crane are to be seen the copper sheets on which the thin sheets used as starting sheets for cathodes are made. In the centre of the picture, workmen are shown removing these thin sheets from the blanks on which the thin sheets are grown, and in the foreground at the lower portion of the picture may be seen stacks of these thin sheets awaiting flattening and the addition of loops by which they are hung in the electrolytic tanks.

Another electrolytic preparation of extreme importance to Australia is the production of aluminium by the electrolysis of alumina, (Al_2O_3) dissolved in molten cryolite $(\text{Na}_3\text{AlF}_6)$ using graphite electrodes. The account of how Charles Martin Hall, an American, who at the age of 22 in 1886 made aluminium by



CHARLES MARTIN HALL
(1863-1914)

this process is a lesson in determination and perseverance. After his professor had told Hall and his classmates of the benefit to the world that a discovery of an efficient method of producing aluminium would have, Hall exclaimed, 'I'm going for that metal'. He tried various methods in vain and then he finally turned his mind to the idea that electricity might help get aluminium out of its ores.

Hall spent months in his shed experimenting with batteries, cups and tumblers borrowed from his professor and he even chopped the wood to cast his own zinc plates for his batteries. At last in February 1886 after six months of frustration, Hall came to the professor's office with a dozen little globules of aluminium in the palm of his hand from his newly discovered process we still use today.

Electroplating

The four essential features of electroplating include;

- (1) the selection of a piece of the pure metal that you want to plate out (this is used as the anode),
- (2) the use of a solution containing the ion of this metal,
- (3) the use of the object to be plated as the cathode, and

- (4) the decomposition of the plating metal on the object using a direct current source.

To ensure good adherence of the plating, the object should be cleaned free of any oxides using acid, any grease films using an alkali, and then finally washed, before being connected as the cathode to a steady, low voltage, direct current source. In figure 16 a method of copper plating is shown, with the main features of electroplating indicated.

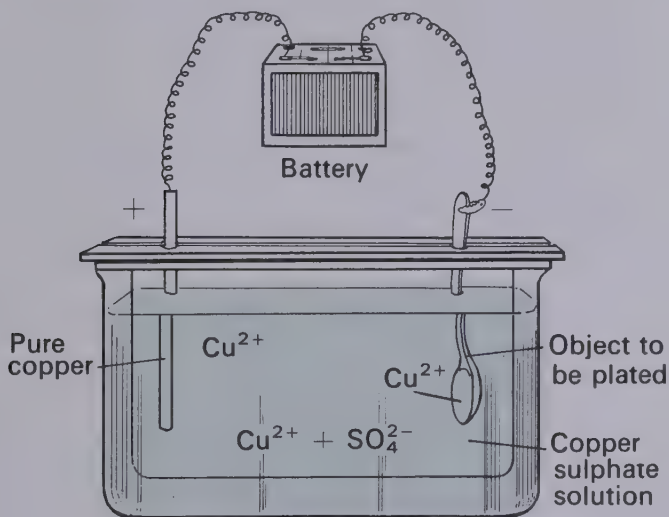
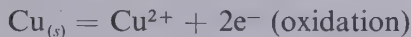
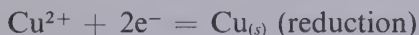


Figure 16. Copper plating an object

At the anode the atoms of copper show a more positive potential to lose electrons and move into solution as ions.



These electrons move around to the cathode where Cu^{2+} ions from the anode and from the electrolyte gain electrons and deposit on the object as copper atoms.



Silver and gold plating is another important industrial process. Solutions such as potassium silver cyanide and potassium gold cyanide can be used as electrolytes with the anodes being pure silver or gold.

Quantitative Relations in Electrolysis

When Michael Faraday first performed his electrolysis experiments in the early 1830s, the atomic theory of John Dalton had been proposed, but no one had yet suggested the existence of electrons. Faraday observed that the quantity of electricity necessary to deposit a given amount of an element such as copper onto an electrode, from solutions of different compounds, such as cupric sulphate CuSO_4 , cupric nitrate $\text{Cu}(\text{NO}_3)_2$, cupric acetate, $\text{Cu}(\text{CH}_3\text{COO})_2$, was always equal to a constant, or some simple multiple of this constant. Electricity, like atoms, seemed to come only in packages.

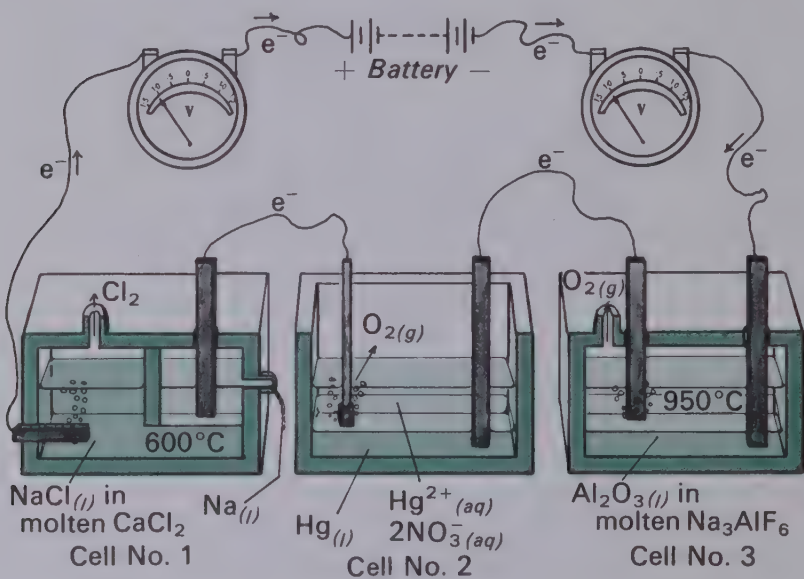


Figure 17. Three different elements—sodium, mercury and aluminium—are deposited at the cathode in each cell by a given amount of electricity

Figure 17 shows three electrolyte systems of great industrial importance. These cells are connected electrically and when the switch is closed electrons flow in the circuit. The two ammeters have the same reading showing that the current entering the cell on the right will be the same as the current leaving the cell on the left, that is, the same number of electrons move through each cell per unit time.

The charge on the electron is 1.6×10^{-19} coulomb, so one mole of electrons would carry a total charge of

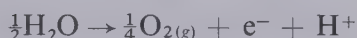
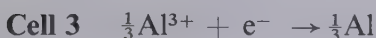
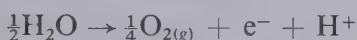
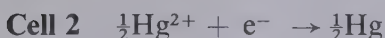
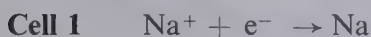
$$(6.0 \times 10^{23} \text{ electrons mole}^{-1}) \times (1.6 \times 10^{-19} \text{ coulomb electron}^{-1}) \\ = 9.6 \times 10^4 \text{ coulombs mole}^{-1}$$

Using more precise measurements a value of 96,454 coulombs per mole of electrons is obtained. This number is called the 'Faraday' in recognition of Michael Faraday's original work on electrolysis.

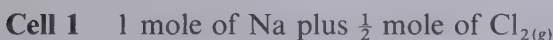
The equations for the half-reactions show what is taking place at the electrodes in each cell.

Cathode reactions

Anode reactions



When one Faraday (9.6×10^4 coulombs) of electricity pass through this circuit, one mole of electrons moves through each of the three cells and produces in



The rate of flow of electrons is defined as the current and is specified by coulombs per second—a rate of one coulomb per second is called one *ampere* (amp) of current.

Now suppose that through each of the three electrolytic cells in figure 17 a current of 4.0 amps flows for 3 hours 20 minutes (200 minutes). The number of coulombs can be calculated.

$$\begin{aligned} \text{Coulombs} &= (\text{current in amps}) \times (\text{time in seconds}) \\ &= 4.0 \times 200 \times 60 \\ &= 4.8 \times 10^4 \end{aligned}$$

$$\begin{aligned} \text{Number of moles of electrons} &= \frac{4.8 \times 10^4 \text{ coulombs}}{9.6 \times 10^4 \text{ coulombs mole}^{-1}} \\ &= 0.5 \text{ mole} \end{aligned}$$

From the electrode reactions and knowing the number of moles of electrons involved, the mass of each product can be calculated.

Cell 1

Anode mass of $\text{Cl}_2 =$

$$0.5 \text{ mole electrons} \times \frac{\frac{1}{2} \text{ mole } \text{Cl}_2}{1 \text{ mole electrons}} \times \frac{71\text{g}}{1 \text{ mole } \text{Cl}_2} = 17.8\text{g}$$

Cathode mass of $\text{Na} =$

$$0.5 \text{ mole electrons} \times \frac{1 \text{ mole Na}}{1 \text{ mole electrons}} \times \frac{23\text{g}}{1 \text{ mole Na}} = 11.5\text{g}$$

Cell 2

Anode mass of $\text{O}_2 =$

$$0.5 \text{ mole electrons} \times \frac{\frac{1}{4} \text{ mole } \text{O}_2}{1 \text{ mole electrons}} \times \frac{32\text{g}}{1 \text{ mole } \text{O}_2} = 4.0\text{g}$$

Cathode mass of $\text{Hg} =$

$$0.5 \text{ mole electrons} \times \frac{\frac{1}{2} \text{ mole Hg}}{1 \text{ mole electrons}} \times \frac{201\text{g}}{1 \text{ mole Hg}} = 50\text{g}$$

Cell 3

Anode mass of O_2 (as in Cell 2)

Cathode mass of $\text{Al} =$

$$0.5 \text{ mole electrons} \times \frac{\frac{1}{3} \text{ mole Al}}{1 \text{ mole electrons}} \times \frac{27\text{g}}{1 \text{ mole Al}} = 4.5\text{g}$$

Redox—The Present and Future

In Australia, a country rich in mineral deposits, there has been, and will continue to be, tremendous interest, research and development into the most efficient and effective ways of extracting metals from their ores. Large companies such as ICI, ALCOA, and BHP have built thriving industries around the reduction of sodium chloride and aluminium ores in electrolytic cells and the reduction of iron, lead and zinc ores using chemical reductants. Optimum operating conditions and the development of new materials in these processes are continually sought after. As an example, the use of platinised titanium as an electrode material rather than carbon, which is oxidised away rapidly, is one of the latest experiments. Although extremely expensive this new material has a very long life compared with carbon and hence its use in many new electrolytic cells.

There is also much research at the moment on the manufacture of electrochemical cells. The efficiency and miniaturization of such cells is important in this age of satellites and transistors. Fuel cells, in which the fuel (usually in the form of a gas) is fed to one electrode and the oxidant to the other, open exciting possibilities for the future production of electricity on a large scale.

Industry concerned with the protection of metal surfaces from nature's oxidation is also continually looking for better ways of doing the job. We are all familiar with galvanized iron and anodized aluminium, but now the latest is 'self painting' steel which protects itself by forming a corrosion resistant compound on its surface after years of exposure to the elements.

One can only wonder as to the new problems man will face and to the new applications he will discover in the challenging world of oxidation-reduction chemistry.

Reading List

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Parry, R. *et al.* *Chemistry Experimental Foundations*. Prentice-Hall, 1970. Ch. 14. A concise, thorough and modern approach to redox chemistry.

Stranks, D. R. *et al.* *Chemistry, a Structural View*. Melbourne University Press, 1965. Ch. 17. Good background reading and well-designed questions.

Toon, E. R. *et al.* *Foundations of Chemistry*. Holt, Rinehart and Winston, 1968.

Questions and Problems

- 1 Complete the following statements.
 "In the process of oxidation
 (a) there is a in oxidation number of one of the atoms in the oxidiser.'
 (b) the oxidiser itself is'
 (c) the oxidiser electrons.'

- 2 State the oxidation number of the underlined elements in the following:
 (a) compounds CrO₃, HNO₃, FeSO₄, HClO₄, MnO₂, Na₂Cr₂O₇, PH₃, ZnSO₄, Na₃PO₄.
 (b) ions CrO₄²⁻, S₂O₈²⁻, AsO₄³⁻, HCO₃⁻, XeO₆⁴⁻.

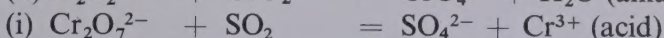
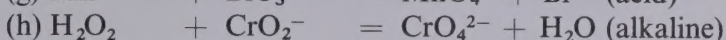
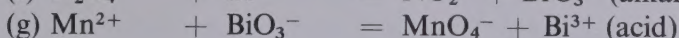
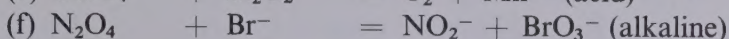
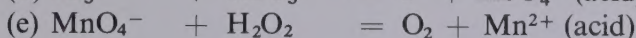
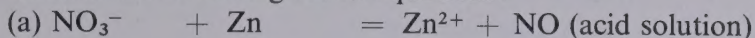
- 3 Suggest a likely product formed by the following oxidants:
 MnO₂, Cl₂, IO₃⁻, H₂O₂, ClO⁻.

- 4 Suggest a likely product formed by the following reductants:
 SO₂, Cu, H₂O₂, Br⁻, CrO₂⁻, AsO₃³⁻.

- 5 Write balanced half equations for:
 (1) BrO⁻ → Br⁻ (alkaline)
 (2) NO₃⁻ → N₂O (acid)
 (3) Bi₂O₃ → BiO₃⁻ (alkaline)
 (4) H₂S → S (alkaline)
 (5) MnO₄⁻ → MnO₂ (acid)
 (6) NO₂⁻ → NO₃⁻ (acid)
 (7) C₂O₄²⁻ → CO₂ (acid)
 (8) HSO₃⁻ → HSO₄⁻ (acid)

- 6 Which of the following are not redox reactions?
 (a) 4NH₃ + 5O₂ = 4NO + 6H₂O
 (b) Zn + 2H₃O⁺ = Zn²⁺ + H₂ + 2H₂O
 (c) Cr₂O₇²⁻ + 2OH⁻ = 2CrO₄²⁻ + H₂O
 (d) PI₃ + 3H₂O = H₃PO₃ + 3HI
 (e) 2Na + 2H₂O = 2NaOH + H₂
 (f) CuSO₄ + 4NH₃ = Cu(NH₃)₄SO₄

7 Balance the following redox equations:



8 Identify (a) the oxidant (b) oxidation in each of the reactions in Question 7.

9 Explain why a piece of iron forms iron (III) chloride when burnt in chlorine and yet it forms iron (II) sulphate when placed in sulphuric acid. Hence explain why ferrous (iron II) salts are generally unstable in air.

10 The standard oxidation potential for magnesium $E^\circ (\text{Mg}/\text{Mg}^{2+}) = +2.37\text{v}$. What precisely does this mean?

11 $E^\circ (\text{Cl}^-/\text{Cl}_2)$ for the reaction

$2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$ is -1.36 volts while the $E^\circ (\text{Fe}/\text{Fe}^{2+})$ for the reaction

$\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$ is $+0.44$ volt.

Draw a labelled diagram of these two standard cells bridged together using a voltmeter and salt bridge, and on the diagram show;

(a) the direction of electron flow,

(b) where oxidation occurs,

(c) the theoretical voltage of the cell,

(d) the direction of movement of the ions in the bridge,

(e) the products formed at each electrode.

12 $E^\circ (\text{Zn}/\text{Zn}^{2+})$ is $+0.76$ volt, $E^\circ (\text{Cl}^-/\text{Cl}_2)$ is 1.36 volts.

$E^\circ (\text{Fe}/\text{Fe}^{2+})$ is $+0.44$ volt, $E^\circ (\text{Br}^-/\text{Br}_2)$ is -1.06 volts.

Use these E° values to predict the likelihood of a reaction between;

(a) iron and zinc sulphate solution,

(b) chlorine and sodium bromide solution.

- 13 Use E° values to explain why copper cannot displace hydrogen gas from nitric acid solution.
- 14 Use E° values to predict the products formed at the electrodes during the electrolysis of
- (1) copper bromide solution (inert electrodes),
 - (2) sodium fluoride solution (inert electrodes),
 - (3) molten magnesium chloride (inert electrodes).
- 15 In the electrolysis of aqueous cupric chloride (CuCl_2), 0.600g of copper is deposited at one electrode. How many grams of chlorine are formed at the other electrode? Write the anode and cathode half-reactions.
- 16 Suppose chemists had chosen the reference reaction to be $2\text{I}^- \rightarrow \text{I}_2 + 2\text{e}^-$ with zero potential as the standard and not the hydrogen electrode,
- (a) What would E° have been for $\text{K} \rightarrow \text{K}^+ + \text{e}^-$?
 - (b) How much would the total potential (E_{total}) have changed for the reaction $2\text{K} + \text{I}_2 \rightarrow 2\text{K}^+ + 2\text{I}^-$?

Index

<i>Key-word</i>	<i>Page</i>	<i>Key-word</i>	<i>Page</i>
acceptor, electron	3	Galvani, L.	15
ampere (amp)	41		
anode	17	Hall, C. M.	37, 38
auto-oxidation	8	ion	31
calyx	1		
cathode	17	Lavoisier, A.	1
cells—Daniell	16		
—primary	29	oxidation number	4-8
—secondary	29, 30	— rules	6
—standard gaseous half	18	oxidation potential	21, 22
—standard metallic half	17	oxidising agent	3
—standard solution half	18		
conjugate pairs, redox	9	phlogiston	1
		potential — oxidation	21, 22
Daniell, J.	16	potential — reduction	21, 23
Daniell cell	16	potential — standard	
Davy, H.	33	electrode	21, 24
disproportionation	8	primary cell	29
donor—electron	3		
		redox	3
electrode potentials,		redox conjugate pair	9
standard	19-25	redox couples	9
electrolysis	31	redox reactions	9
—of gaseous solutions	33	reduction potential	21, 23
electrolyte	31		
electron acceptor	3	secondary cell	29, 30
electron donor	3	standard electrode potential	21
electron transfer		standard gaseous half cell	18
electroplating	38, 39	standard metallic half-cell	17
		standard solution half-cell	18
Faraday, M.	31		
faraday, the	41	Volta, A.	15

A 13736



After completing his B.Sc. and Diploma of Education at the University of Adelaide and the Adelaide Teachers College, J. S. Langrehr began teaching chemistry, in 1960, at Findon High School, South Australia, where he is at present senior science master.

During the eleven years of his teaching career he has been a member of the South Australian Public Examination Board Chemistry Committee, as well as the S.A. Education Department Chemistry Advisory Curriculum Committee. He is also a member of the S.A. Science Teachers Association.

In 1965 he was selected as an Australian Fulbright Exchange Teacher. This enabled him to teach chemistry in a New York state school system for a year, to attend the National Science Teachers Convention in New York City and to visit many universities and schools along the north-east coast of the U.S.A.

As a result of this visit, he became very interested in the field of Instructional Technology and Educational TV, and returned to the U.S.A. during 1969-70 to gain further experience and ideas in these areas.

Mr Langrehr was born and educated in Adelaide and is keenly interested in golf, tennis, swimming, travel and reading.